Interaction of Materials and Plasmas: Spectroscopic Studies of Chemical Phenomena

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I. Introduction

Webster defines ablation as a removal or a carrying away. Thus, the ablation process, as applied to materials, denotes the removal or carrying away of material. To study this process, arc jets or plasma jets have been employed as sources to "ablate" samples. Reported here are the results from using various configurations of commercially available plastics. Surface characteristics (e.g., surface temperature, emissivities, and absence or presence of char formation and removal) and plasma interaction (e.g., the formation of gaseous degradation products) have been studied. To accomplish this, emission spectroscopic and spectrographic techniques were employed over the wavelength range 0.2-9.0 μ. Results of measurements on Delrin*, $(-CH_2-O-)_x$, Zelux, $(-C_6H_4-C(CH_3)_2-C_6H_4-O-(C=O)-O-)_x$, and to some extent Teflon, $(-CF_2-CF_2-)_x$, will be cited as illustrative examples.

When heat is applied (in this case from the arc jet), the surface temperature of the materials rises until at some point the ablation process, and not the heating process, becomes the dominant mechanism controlling the chemistry. However, this ablation process can occur in several ways. First, a pseudosublimation may take place at the surface; namely, degradation of the polymer to gaseous products with no resulting surface changes; second, degradation of the polymer which leads to a change to the liquid state with subsequent flowing away of the liquid phase; and third, degradation of the polymer yielding some type of a char which either forms and blows off, or adheres to the model surface. Combinations of the above may also take place. Examples of the various types of ablators are graphite, quartz and Zelux respectively. A good discussion of ablation is given in reference 1.

II. Plasma Jet Characteristics

For the polymeric materials used, the heat inputs (enthalpies) and heat fluxes from the various plasma jets are more than enough to cause ablation to be

*Delrin is the DuPont trade name for Polyoxymethylene, the Celinese Corp. produces this material under the tradename Celcon. Lexan is a commercially available polymer resin which in the final, fabricated form is known as the plastic Zelux.

[1] M.C. Adams, ARS J, 29, 625 (1959).

the dominant decomposition mechanism. One type of plasma jet employed is of the same type as that described by Watson, Ferguson, and Nicholls.[2] Another type is similar except that a plenum chamber (for adding gas downstream and thus being able to produce simulated air) was used. The electrodes are of the nonerod-ing type (a copper anode and a thoriated tungsten cathode).

Although the plasma jets are not in complete thermal equilibrium, the approach to equilibrium is much closer here than in glow discharges at the same pressure.

With nitrogen as the propellant gas, the arc power was of the order of 25 kw while the enthalpy (H/RT) was 220 (7392 Btu/lb).

III. Experimental Techniques

It is possible, with infrared techniques, to follow the surface behavior of plastic materials when they are subjected to the plasma jets by determining sur-face temperatures as a function of time, and surface temperature and emissivity as a function of wavelength. Dramatic changes in surface temperature will also give an indication of char formation and propagation. To carry out these measure-ments, a CaF_2 or NaCl prism was used in a Littrow configuration which was coupled with a Au-doped Ge detector chopped at 690 cps. The spectra or other traces were displayed on a Tektronix Type 502 oscilloscope by sweeping the scope at the desired rate. For time histories, the wavelength is kept fixed. For spec-tral scans, the Littrow mount is driven by a cam which oscillates the mount and scans the desired $\Delta\lambda$ every 0.2 second. For wavelength calibration, a helipot is attached to the Littrow arm and a periodic wave is displayed on one beam of a dual-beam oscilloscope; the signal output is displayed on the other. A Barnes black-body is used to give absolute temperature calibration.

For all visible and ultraviolet results, the spectra were recorded photo-graphically on a Hilger E498 (all quartz) or E528 (quartz and glass employing quartz optics) using Kodak 103-F plates. The F plates were used because the widest wavelength coverage (0.23 to 0.70 μ) could be obtained without serious loss of sensitivity.

The IR gaseous spectra (0.8 to 1.5 μ) were taken with a single pass mono-chrometer employing an SiO_2 prism and PbS detector and were recorded on a dual-beam oscilloscope (signal output on one beam and drum number readings on the other).

IV. Surface Characteristics

Figure 1 is the room temperature absorption spectrum of Delrin, while figure 2 is the emission spectrum (2 to 7 μ) for a Delrin sample ablating in a nitro-gen plasma jet. Note the strong absorption and emission in the 3.3 μ region and beyond 7μ while there is weaker absorption and emission in the 4.0 to 6.5 μ re-gions. Thus, from figure 2, we have determined the surface temperature of Delrin at λ = 3.3μ to be 725 ± 10°K. The approach used to deduce the surface

[2] M.D. Watson, H.I.S. Ferguson, R.W. Nicholls, Can J. Phys., 14, 1405 (1963).

temperature was to compare the absolute radiant emittance obtained with that from a calibrated blackbody in a spectral region where the assumption of the emissivity, ϵ, near unity is valid. This assumption in turn, is based on transmission measurements of absorption spectra of thin films to determine the wavelengths where the absorptivity is so large that the emissivity also must be near one; i.e., Kirchhoff's Law is invoked. This assumption of near unit emissivity is most uncertain in the case of charred materials where often the reflectivity can be high in the infrared.

With a heavy char former such as Zelux, the surface temperature varies quite widely with time, so in order to watch this behavior a constant wavelength is picked and the behavior is scanned as a function of time. Figure 3 gives the IR emission from ablating Delrin and figure 4 gives the IR emission from ablating Zelux; both taken at $\lambda = 3.4\mu$. The big difference between the heavy char former (Zelux) and the non-char former (Delrin) is readily apparent when the two figures are compared. The spikes in figure 4 show the super-heating and blowing off of the char layer.

Figure 3 will also illustrate another point. Note that in the beginning (up to 1/2 second) the voltage rises very rapidly and then changes slope. We have called this point the "breakpoint" and ascribe it as the point where the rate of ablation has become large enough to control the surface temperature. For a number of materials, the breakpoint temperature obtained from these plasma jet measurements has been correlated with those obtained from thermogravimetric analysis (TGA) decomposition experiments. One such experiment for Delrin in air is illustrated in figure 5. For Delrin, we measure the breakpoint temperature as 593 ± 10°K, and from TGA, the temperature for 100 percent decomposition is 605°K. Because of char formation, the heavy char formers do not usually yield a well defined breakpoint (note figure 4).

V. Gaseous Products

The sample configurations used to date to obtain gaseous spectra are pipes and cones. The pipes are 4-1/2 inches long and 2 inches in diameter. The hole through which the gas flows is initially 1 inch in diameter. Because of the nature of the jet, the flow through the pipe is laminar. The cones employed have 1-inch base diameters and an included angle of 20 degrees. When the plasma interacts with the cone, a shock wave is set up and the region between the shock envelope and the surface consists of high temperature gas highly contaminated with ablation products, and as an emission source has considerable intensity.

Figures 6, 7, and 8 are spectra of a Zelux pipe in a Helium jet, a Zelux pipe in a nitrogen jet, and a Zelux cone in a nitrogen jet, respectively. Table I is a compilation of the species identified as present and illustrates the effect of a change in the plasma gas and in the sample configuration. The helium plasma jet produces a hotter jet (higher gas temperature) than the nitrogen jet while the effect of a higher temperature due to shock wave effects can be seen by comparing figures 7 and 8.

A close examination of figure 8 shows that three of the dominant radiating species in the visible are CN, CH, C_2. Kokline[3] firing preheated Zelux models at 16,000 ft/sec in a ballistic range also finds the three predominant visible radiators as CN, CH and C_2. Thus, although two widely different experimental media have been used, under the proper conditions there is correlation in the results obtained. In this way, one sees that plasma jet results can point the way to, and act as, a starting point for more sophisticated experiments. One such experimental medium is the shock tube. In noting the various species that are formed during degradation of a plastic in a plasma jet, mixtures of gases which, when shocked, will yield the appropriate species, can then be studied by simultaneously monitoring the important wavelengths. With a drum camera, it would be possible to monitor variations in the behavior of some species in the visible region. One advantage of the plasma jet is the large test time one has when compared with ballistic ranges and shock tubes.

Infrared measurements in the 0.8 to 2.0 micron region showed strong gas radiation characteristic of the CN red system when a Zelux model ablated in a nitrogen arc. A similar scan of the nitrogen jet without any model produces the first positive system of nitrogen, but at a much lower intensity level.

Figure 9 is the spectrum obtained when a Teflon model ablates in an Argon plasma jet. The principal diatomic, UV radiator is CF along with some continuum radiation. The CF spectrum that is produced is quite pure and avoids many of the impurities (e.g., CF_2, S) encountered by other investigators. The relatively short test times needed to obtain decent intensity compared with other methods (e.g., flames) is well illustrated. Thus, by picking the proper material and arc gas, one can obtain and study, relatively easily, high temperature diatomic species.

VI. Acknowledgment

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The authors acknowledge with appreciation the advice and help of many individuals at RAD during the course of this work and to Dr. T. Marshall for reading and commenting on this manuscript.

[3] A. Dmitrieff-Kokline, Spectrographic Studies of the Radiation Emitted by Hypersonic Projectiles, Canadian Armament Research and Development Establishment, TN-1564, May, 1963.

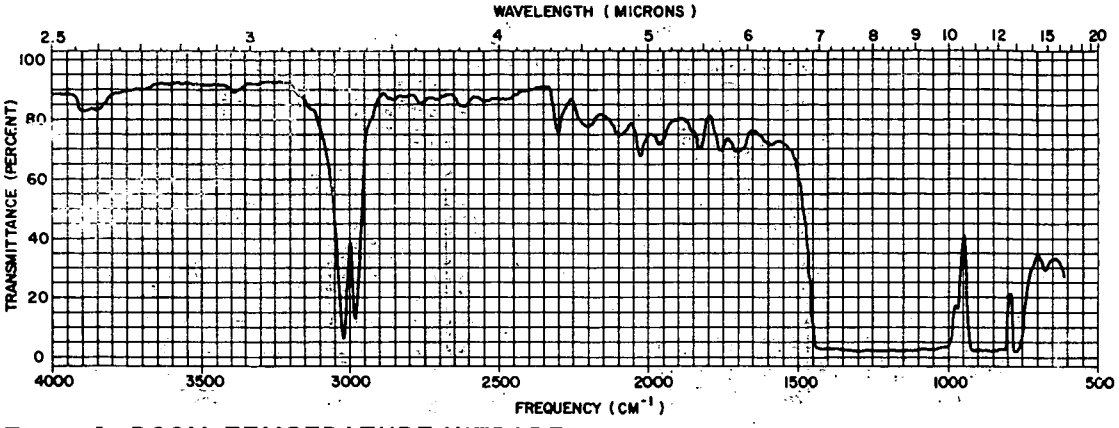


Figure 1 ROOM-TEMPERATURE INFRARED ABSORPTION SPECTRUM OF DELRIN (0.003-inch Film)

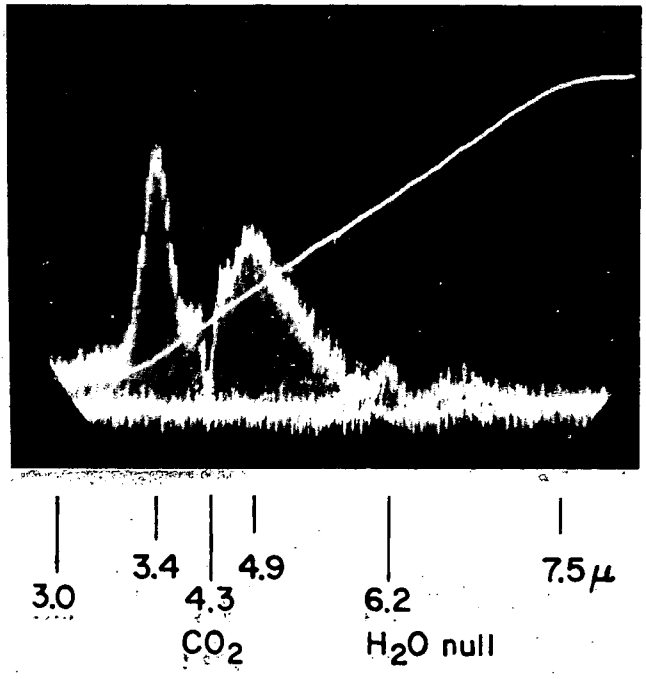
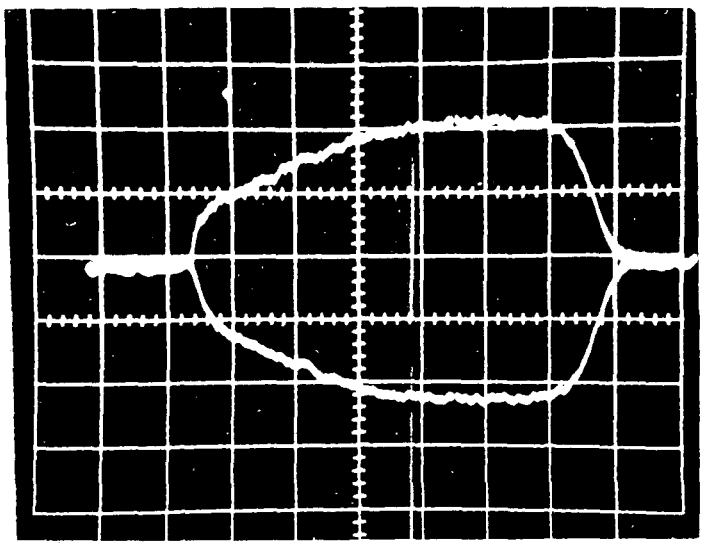
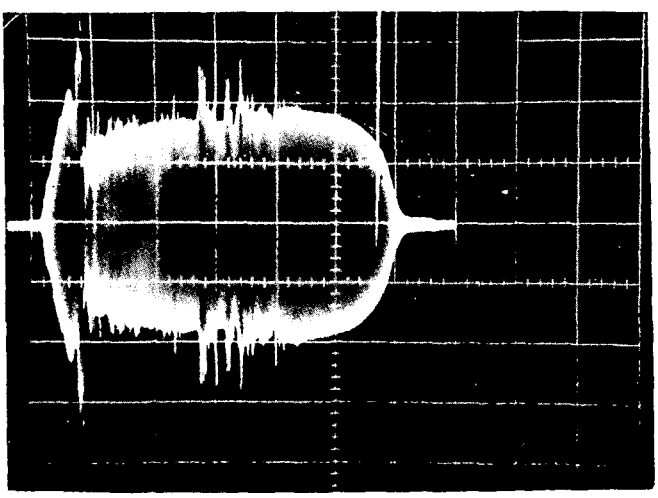


Figure 2 DELRIN INFRARED EMISSION SPECTRUM (0.5 V/cm)



(λ = 3.4 MICRONS)



64-1245 Figure 4 INFRARED EMISSION HISTORY OF ABLATING ZELUX
(λ = 3.4 MICRONS, 5 SEC/CM SWEEP)

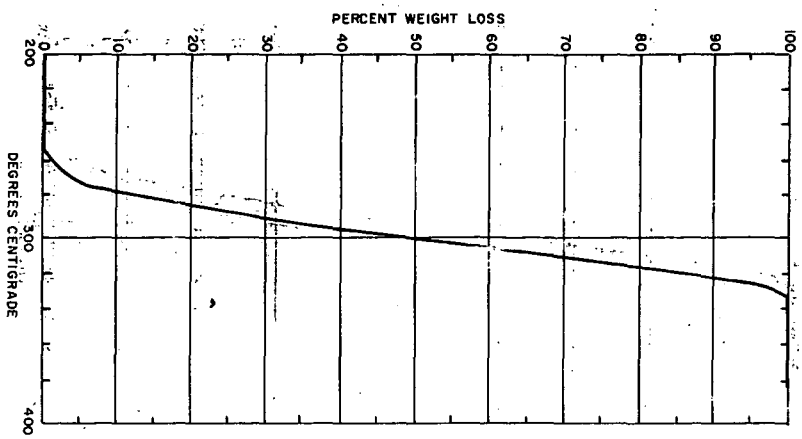


Figure 5 THERMOGRAVIMETRIC ANALYSIS, DELRIN IN AIR

ZELUX PIPE/HELIUM
2300 A

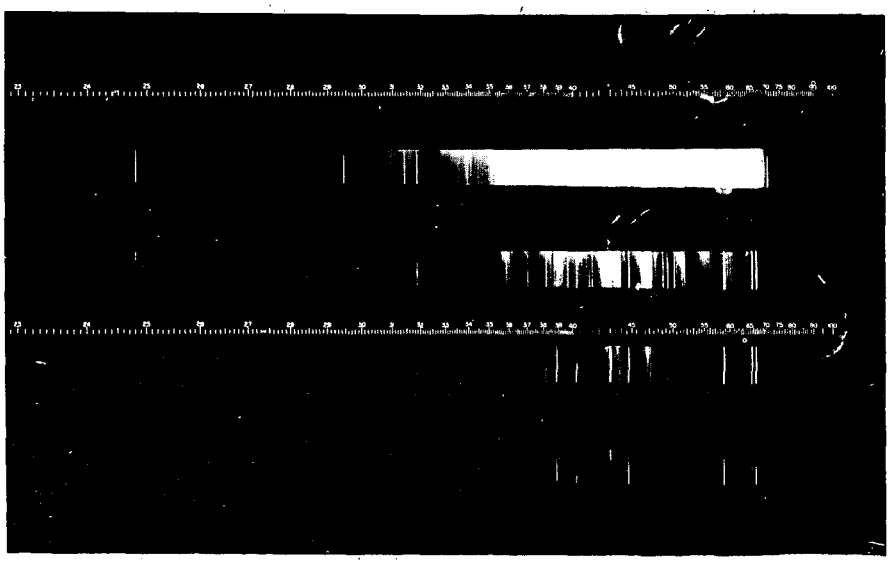
a NO ARC SPECTRUM

b Sw, 10 SECONDS

c Sw, 1 SECOND

d Sw, 1/5 SECOND

e Sw, 1/25 SECOND



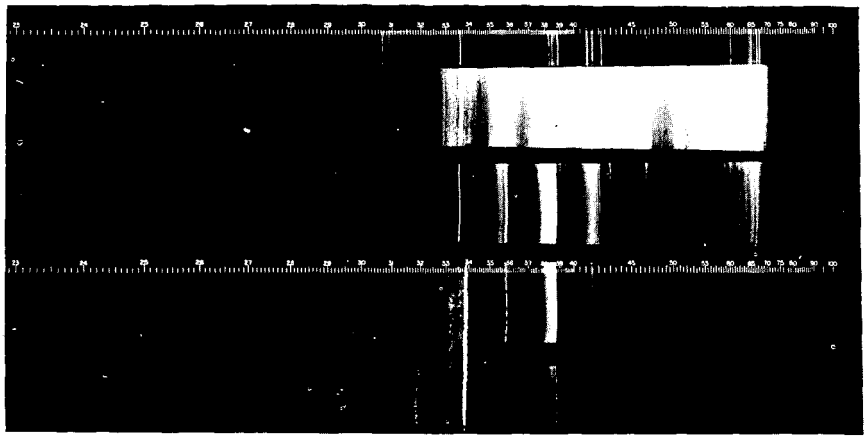
Sw = 60-micron slit
EXPOSURE TIMES AS GIVEN; a PLUME ONLY;
b THROUGH e WITH MODEL IN STREAM

63-7171

Figure 6 ZELUX PIPE -- HELIUM

ZELUX PIPE / NITROGEN
2300A

a Sw, 10 SECONDS
b Sw, 10 SECONDS
c Sw, 1 SECOND
d Sw, 1/5 SECOND
e Sw, 1/25 SECOND

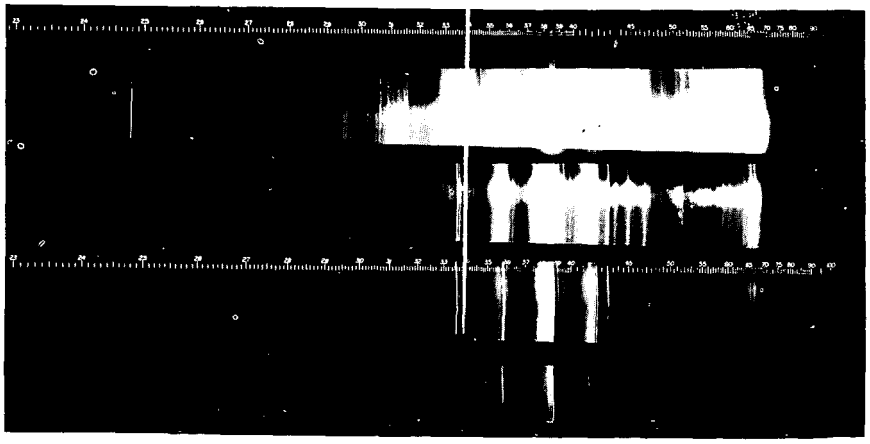


Sw = 60-MICRON SLIT
EXPOSURE TIMES AS GIVE; a PLUME ONLY;
b THROUGH e WITH MODEL IN STREAM

Figure 7 ZELUX PIPE -- NITROGEN

ZELUX CONE / NITROGEN
2300A

a Sw, 1 SECOND
b Sw, 10 SECONDS
c Sw, 1 SECOND
d Sw, 1/5 SECOND
e Sw, 1/25 SECOND



Sw = 60-MICRON SLIT
EXPOSURE TIMES AS GIVE; a PLUME ONLY;
b THROUGH e WITH MODEL IN STREAM

Figure 8 ZELUX CONE -- NITROGEN

TEFLON CONE / ARGON

2200 A

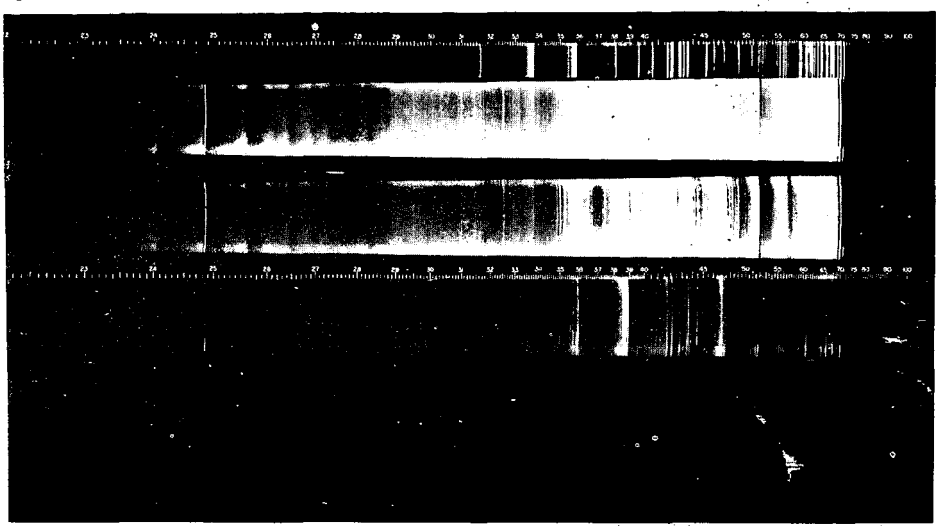
a. Sw, 10 SECONDS

b. Sw, 20 SECONDS

c. Sw, 10 SECONDS

d. Sw, 1 SECOND

e. Sw, 1/5 SECOND



Sw = 60 micron slit
EXPOSURE TIMES AS GIVEN; a PLUME ONLY;
b THROUGH e WITH MODEL IN STREAM

Figure 9 TEFLON CONE -- ARGON

TABLE I

SPECIES IDENTIFIED IN SPECTRA OF ZELUX-CONTAMINATED GASES

ZE Pipe/He (Figure 2)	ZE Pipe/N_2 (Figure 3)	ZE Cone/N_2 (Figure 4)
C (s)[a]	C (m)	C (s)
H (s)	H (w)	H (m)
-	CN (s)	CN (s)
CH (m)	CH (m)	CH (m)
C_2[b] (m)	C_2 (m)	C_2 (m)
-	NH (m-w)	NH (s)

a: s = strong, m = medium, w = weak mean relative intensities from visual estimates of spectral plates.

b: Besides the C_2 Swan systems that are identified, the following C_2 systems (with bandhead values) also are identified as present when ZE pipe is in a helium plasma jet: Fox-Herzberg (heads at 2855, 2987, 3129, and 3283 A), Deslandres-D'Azambula (heads at 3400, 3588, 3607, 3850, 4040, 4060, and 4100 A).